

Structural Stability of Giant Polyoxomolybdate Molecules as Probed by EXAFS

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Received June 26, 2003; accepted November 4, 2003

PACS numbers: 36.40.-c; 36.40.Qv; 61.10.Ht

Abstract

Recent progress in synthesis of “giant” polyoxomolybdate (POM) molecules that have a structure of hollow spheres or wheels and size of several nanometers in diameter has emphasized the need in their accurate structural investigation. Our temperature-dependent EXAFS studies demonstrated that the first generation POM molecules containing 132 Mo atoms, undergo irreversible structural transformations at ca. 500 K, while the recently synthesized second generation POM at ca. 400 K. The number of different structural units in these molecules can be accurately obtained from EXAFS analysis and compared with model structure calculations. In our method of analysis, we use theoretical calculations of pair radial distribution functions from the model structures as initial approximations to analyze the structures of these molecules. Our analysis allowed us to identify the new POM structure as a giant sphere, similar to the $\{Mo_{132}\}$ structure but containing 522 Mo atoms. Our results also demonstrate that the structural rigidity of different building blocks of these molecules can be quantitatively probed by EXAFS.

1. Introduction

In polyoxomolybdate (POM) molecules, that belong to a class of structurally underconstrained systems, a number of fascinating physical properties are expected. For example, in an analogous framework system, ZrW_2O_8 , the presence of “rigid unit modes” (RUMs) was proposed to be the driving force of the recently discovered negative thermal expansion (NTE) [1]. These RUMs are a special class of “floppy modes” that were recently observed in amorphous and crystalline silicates, the transverse acoustic modes of a framework structure composed of rigid SiO_4 tetrahedra [2].

The building blocks of the $\{Mo_{132}\}$ structure can be visualized (Fig. 1) as containing 12 $\{(Mo)Mo_5\}$ pentagons with longer Mo-Mo distances and 30 $\{Mo_2^V O_4\}$ bridges that have shorter Mo-Mo bond lengths [3]. The structural data available from X-ray crystallography were processed by our software program that computes pair radial distribution functions (PRDF) $g_{AB}(r) = dN_{AB}/dr$ for A-B pairs (where element A is a central (absorbing) atom and element B is its neighbor. In the present case, the distributions were calculated for Mo-O and Mo-Mo neighbors. As it will be shown below, these calculations were essential to adequately analyze EXAFS data in the reference $\{Mo_{132}\}$ structure and apply the same analysis procedure to the unknown $\{Mo_N\}$ structure.

2. Synthesis and characterization of the 1st and 2nd generation “giant spheres”

The synthesis of the C_{60} -like $\{Mo_{132}\}$ and another even larger, hollow, spherical POM (likely to have the structure of 2nd generation of C_{60} -like) have been reported in literature [4, 5].

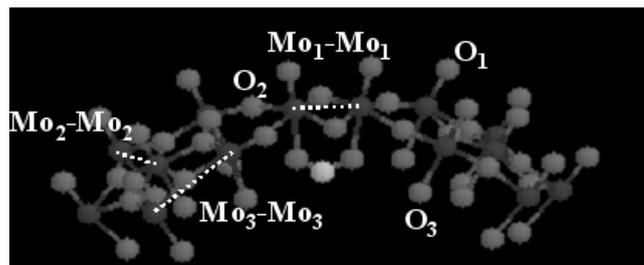


Fig. 1. Building blocks of the $\{Mo_{132}\}$ structure. Shown are $\{(Mo)Mo_5\}$ pentagons that have two types of Mo-Mo bonds: Mo_2-Mo_2 and Mo_3-Mo_3 , and the $\{Mo_2^V O_4\}$ bridges that have the third type of Mo-Mo bonds, denoted as Mo_1-Mo_1 . Shown also are three types of oxygen atoms that belong to three distinct bond types: Mo-O₁, Mo-O₂, and Mo-O₃.

It is very easy to synthesize and grow $\{Mo_{132}\}$ single crystals that can be used for structure determination by single crystal X-ray diffraction experiments. However, for the larger POM, the final products are usually powders or tiny crystals. Small-angle X-ray scattering measurements showed ordered 5.2-nm primitive cubic packing of the single POM molecules, indicating the new POM molecules are extraordinarily large (for comparison, $\{Mo_{132}\}$ has the size of 2.9 nm), but the molecular structure of the new POM cannot be directly determined. We describe here that convincing evidence can be obtained from EXAFS measurements by realizing that the basic building units for various POMs are the same.

3. EXAFS measurements and analysis of the nano-spheres

EXAFS measurements were performed at the beamline X16C of the National Synchrotron Light Source (NSLS). Both types of samples, the $\{Mo_{132}\}$ and the 2nd generation $\{Mo_N\}$ spheres, were measured in transmission at different temperatures (from 140 K to 473 K) under nitrogen flow, using a custom-designed and built catalyst cell. Above ca. 500 K, the $\{Mo_{132}\}$ samples underwent irreversible structural transformations. The onset of the irreversible changes was lower (ca. 400 K) for the $\{Mo_N\}$ samples. Irreversibility was checked by comparing the data measured at 300 K before and after thermal treatment.

Different groups of Mo-O and Mo-Mo bonds can be observed in Fig. 2 that shows raw EXAFS data. Next to the horizontal axis in Fig. 2 (B), the PRDF plots are also shown. Comparison between the r -space data and X-ray crystallography results visualized by the PRDF plots demonstrates that EXAFS contains unique information on each of the structural groups (3 Mo-O groups and 3 Mo-Mo groups, Fig. 1). For example, the peak at ca. 1.2 Å in Fig. 2 (B) corresponds to the Mo-O₁ axial pair in

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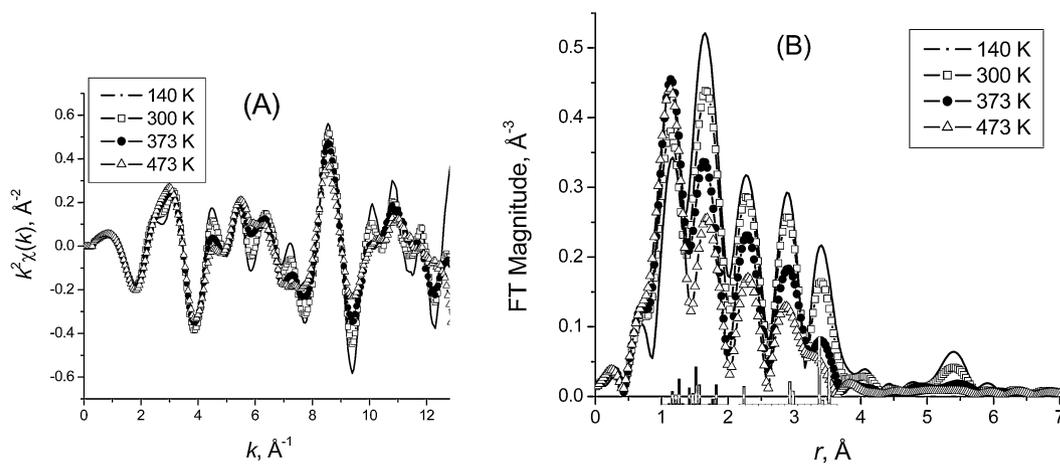


Fig. 2. EXAFS data (in k - and r -spaces) of the $\{\text{Mo}_{132}\}$. The radial distribution functions of Mo-O and Mo-Mo pairs, shifted toward lower r by 0.5 \AA and 0.3 \AA , respectively, are shown next to the horizontal axis in (B).

MoO_6 octahedra. The second peak, at ca. 1.7 \AA corresponds to another axial Mo-O₃ and the equatorial Mo-O₂ bond groups of MoO_6 octahedra. From visual observation (the first peak intensity increases with temperature while that of the second peak decreases with temperature), one can hypothesize that the MoO_6 octahedral environment is not rigid. Rather, it should become progressively distorted at elevated temperatures.

FEFF6 [6] was used to calculate model Mo-O and Mo-Mo theoretical contributions to EXAFS. The theory that included three Mo-O and three Mo-Mo single-scattering paths was fitted to the data in r -space using FEFFIT [7]. The coordination numbers of each type of bond were dictated by the $\{\text{Mo}_{132}\}$ structure and fixed in the fits to be equal to the values obtained by our PRDF calculations. The bond lengths and disorders were varied independently for all bonds. Fit quality is shown in Fig. 3 for the lowest and highest temperatures analyzed.

The EXAFS data in the unknown sample, $\{\text{Mo}_N\}$ (Fig. 4) look strikingly similar to the $\{\text{Mo}_{132}\}$ standard (Fig. 3). Indeed, the peak positions align well for the Mo-O and Mo-Mo bonds between the two samples. Since the r -space data in the case of Mo_{132} structure mimics the PRDF obtained for a spherical particle that has $\{(\text{Mo})\text{Mo}_5\}$ pentagons and $\{\text{Mo}_2\text{O}_4\}$ bridges with characteristic Mo₁-Mo₁, Mo₂-Mo₂ and Mo₃-Mo₃ bond lengths, the fact that

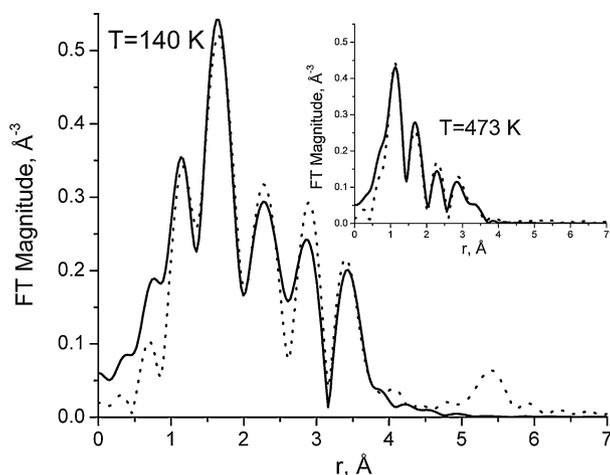


Fig. 3. Fourier transform magnitudes of EXAFS data and fits of the $\{\text{Mo}_{132}\}$ at 140 K and 473 K.

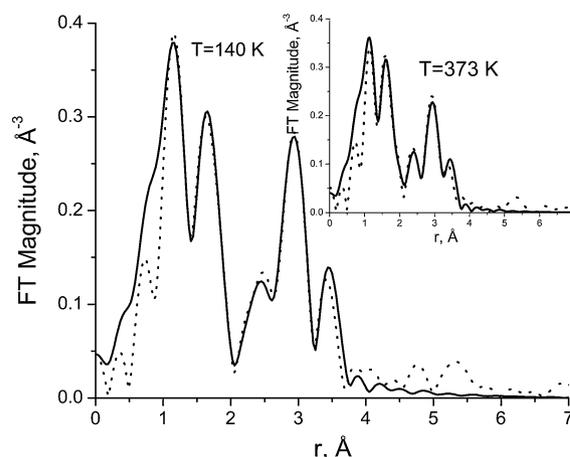


Fig. 4. Fourier transform magnitudes of EXAFS data and fits of the 2nd generation sphere at 140 K and 373 K.

our data for the unknown samples has signatures of the same groups indicates that the topological properties of the two types of particles, $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_N\}$ should be very similar. In literature, one of the possible candidates for a spherical cluster that is larger in size than Mo_{132} is the 522-atom cluster that also has pentagons and bridges like the $\{\text{Mo}_{132}\}$ [8]. That justifies our analysis approach as nearly identical to that of the $\{\text{Mo}_{132}\}$ reference structure: we fixed the coordination numbers of each type of bond in accordance with the $\{\text{Mo}_{522}\}$ structure and varied the bond lengths and their disorders. The data and best fits are shown in Fig. 4 for the lowest and highest temperatures analyzed.

4. Results

σ^2 for the axial Mo-O₁ and Mo-O₃ bonds were found to be almost the same ($\sim 0.004(1) \text{ \AA}^2$) throughout the temperature range (140 K to 473 K). The σ^2 for the equatorial Mo-O₂ bonds increased three-fold from $0.0050(9) \text{ \AA}^2$ to $0.0142(15) \text{ \AA}^2$ in the same temperature range.

The best fit values for the bond lengths for $\{\text{Mo}_{132}\}$ (shown by solid vertical lines in Fig. 5) were consistent with the PRDF calculations. The best fit results obtained in the 2nd generation sphere sample were also consistent with the same distance ranges for the three Mo-O bond groups and three Mo-Mo bond groups (shown by dashed vertical lines in Fig. 5), as in $\{\text{Mo}_{132}\}$ structure.

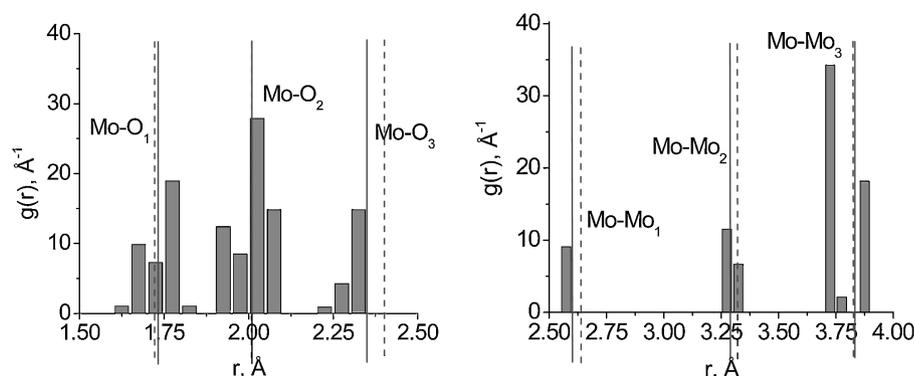


Fig. 5. PRDFs calculated from the crystallography data for Mo-O and Mo-Mo pairs. Shown by vertical lines are the best-fit EXAFS results for each group of distances obtained for the 1st and 2nd generation spheres.

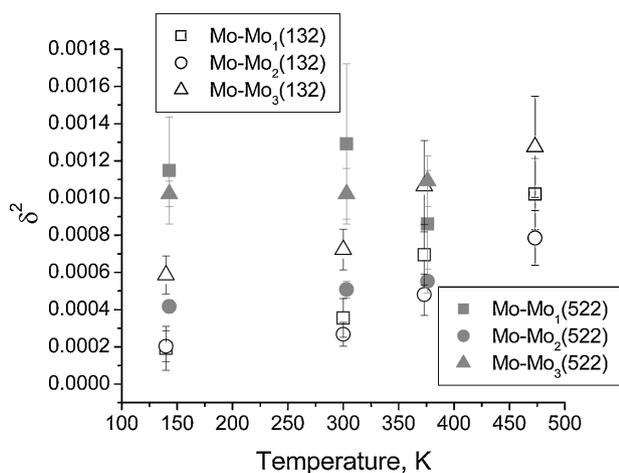


Fig. 6. Bond-length-normalized mean square displacement δ^2 .

Figure 6 shows the normalized bond length disorder parameter, $\delta^2 = \sigma^2/R^2$ (where R is the bond length) that we calculated based on the best fit results obtained for σ^2 for each of the three Mo-Mo bonds in the both samples. The use of δ^2 is preferred because longer bonds may have larger σ^2 than shorter bonds not only due to the longer bonds' larger disorder but also due to the smaller correlation between the vibrations of their atoms. If σ^2 is normalized by R^2 , the ambiguity caused by the Mo-Mo bond length differences in different structures will be partially lifted when the rigidities of the two structures are examined.

5. Discussion and Conclusions

The fit results for σ^2 of Mo-O bonds confirmed our hypothesis that the MoO_6 octahedra are not rigid in $\{\text{Mo}_{132}\}$. From the trend described above we infer that the MoO_6 octahedra are progressively distorted at elevated temperatures. This property has a familiar ring from the NTE materials where an asymmetric "tentpole" distortion of what previously was believed to be a rigid unit, a ZrO_4 tetrahedron, was proposed to be an alternative scenario to transverse O vibration in the W-O-Zr linkages in ZrW_2O_8 [9].

For the structure of the 2nd generation molecule, our results show that the topology of this molecule is analogous to that of

$\{\text{Mo}_{132}\}$, as we assumed based on preliminary visual observation of the data. Because the number of $\text{Mo}^{\text{V}}\text{-Mo}^{\text{V}}$ bonds (denoted by $\text{Mo}_1\text{-Mo}_1$ in Fig. 1) is much larger in this molecule (as determined by UV/vis. spectrometry, $\sim 87 \pm 8\%$ of Mo atoms in the POM are Mo^{VI} , compared to 55% in $\{\text{Mo}_{132}\}$) than in $\{\text{Mo}_{132}\}$, and due to the uniqueness of the topological characteristics of various POMs, the structure of this molecule must be that of $\{\text{Mo}_{522}\}$.

The non-monolithic nature of POMs has been discussed previously. As pointed out by A. Müller, *et al.* [10], most POMs consist of different $\{\text{MO}_x\}$ -type building-block units that are highly stable. However, the linkages that connect these building blocks directly or via other coordinating centers [10] may be fragile and break even at moderate temperatures. As predicted by the different stability ranges of temperature in the $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{522}\}$ molecules, their structural rigidities should be different. Our EXAFS results indicate that the dominating factor responsible for this effect is the rigidity of the $\text{Mo}^{\text{V}}\text{-Mo}^{\text{V}}$ bridges that connect the building blocks in these two structures. Figure 6 demonstrates that in Mo_{132} , these bridges are less disordered and therefore, more stiff than in Mo_{522} . We believe that the relative rigidity of these bond types, which serve as bridges between the $\{(\text{Mo})\text{Mo}_5\}$ pentagon building blocks, revealed in our analysis of $\{\text{Mo}_{132}\}$ EXAFS data is the origin of these molecules' enhanced stability over the $\{\text{Mo}_{522}\}$ particles.

Acknowledgment

AIF and SCF were supported by Yeshiva University Research Foundation. TL acknowledges support by the U.S. Department of Energy, Division of Materials Science, No. DE-AC02-98CH10886. NSLS is supported by the U.S. Department of Energy.

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